

- -- 26. A composition for the oxidation dyeing of keratin fibers comprising:
- a) at least one oxidation base, and
- b) as direct dye, at least one 3-aminopyridine derivative chosen from the compounds of formula (I):

$$N = N - A \qquad (I)$$

$$R_1 \qquad B \qquad R_4 \qquad R_3$$

in which:

- B is chosen from formula (la) and (lb):

$$\bigvee_{O}^{N^+} (la) \qquad \bigvee_{R}^{N^+} X^- (lb)$$

- R is a C₁-C₄ alkyl radical;

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- R₁ is chosen from a hydrogen atom, a halogen atom, a C₁-C₄ alkyl radical, and a
 C₁-C₄ alkoxy radical;
- R₂ is chosen from a hydrogen atom, a C₁-C₄ alkyl radical, and a C₁-C₄ alkoxy radical;
- R₄ is chosen from a hydrogen atom, a halogen atom, a C₁-C₄ alkyl radical, a nitro, an amino radical and a (C₁-C₄)acylamino radical;
- R₃ is a hydrogen atom, or R₄ and R₃ together form a 6-membered unsaturated ring bearing a hydroxyl substituent chelated with one of the nitrogen atoms of the azo double bond;
- A is a residue -NR₅R₆ in which R₅ is chosen from a hydrogen atom, a C₁-C₄ alkyl radical, a C₁-C₄ monohydroxyalkyl radical and C₂-C₄ polyhydroxyalkyl radical and R₆ is chosen from a hydrogen atom, a C₁-C₄ alkyl radical, a C₁-C₄ monohydroxyalkyl radical, a C₂-C₄ polyhydroxyalkyl radical, a phenyl ring and a -CH₂-SO₃Na radical;
- X is chosen from a monovalent anion and a divalent anion, and
- c) at least one coupler chosen from a meta-aminophenol derivative of formula (II), and an addition salt thereof with an acid:

in which:

- R₇ is chosen from a hydrogen atom, a C₁-C₄ alkyl radical, a C₁-C₄ monohydroxyalkyl radical, a C₂-C₄ polyhydroxyalkyl radical and a C₁-C₄ monoaminoalkyl radical;
- R₈ is chosen from a hydrogen atom, a halogen atom, a C₁-C₄ alkyl radical, and a
 C₁-C₄ alkoxy radical;
- R₉ and R'₉, which are identical or different, are chosen from a hydrogen atom, a halogen atom, a C₁-C₄ alkyl radical, a C₁-C₄ alkoxy radical, a C₁-C₄ monohydroxyalkyl radical, a C₂-C₄ polyhydroxyalkyl radical, a C₁-C₄ monohydroxyalkoxy radical and a C₂-C₄ polyhydroxyalkoxy radical;

with the proviso that at least one of the substituents R_7 , R_8 , R_9 and R'_9 is not a hydrogen atom.

- 27. A composition according to Claim 26, wherein said keratin fibres are human keratin fibres.
- 28. A composition according to Claim 27, wherein said human keratin fibres are human hair.
- 29. A composition according to Claim 26, wherein said halogen atom is chosen from chlorine, bromine and fluorine.
- 30. A composition according to Claim 26, wherein said X^- is chosen from a halogen atom, a hydroxide, a hydrogen sulfate and a (C_1-C_6) alkyl sulfate.

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- 31. A composition according to Claim 30, wherein said halogen atom is chosen from chlorine, bromine, fluorine and iodine.
- 32. A composition according to Claim 30, wherein said (C_1-C_6) alkyl sulfate is chosen from a methyl sulfate and an ethyl sulfate.
- 33. A composition according to Claim 26, wherein said at least one oxidation base is chosen from a para-phenylenediamine, a double base, a para-aminophenol, an ortho-aminophenol and heterocyclic oxidation bases.
- 34. A composition according to Claim 33, wherein said para-phenylenediamine is chosen from a compound of formula (III), and an addition salt thereof with an acid:

in which:

R₁₀ is chosen from a hydrogen atom, a C₁-C₄ alkyl radical, a C₁-C₄ monohydroxyalkyl radical, a C₂-C₄ polyhydroxyalkyl radical, a (C₁-C₄)alkoxy(C₁-C₄)alkyl radical, a C₁-C₄ alkyl radical substituted with a nitrogenous group, phenyl and 4'-aminophenyl;

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- R₁₁ is chosen from a hydrogen atom, a C₁-C₄ alkyl radical, a C₁-C₄ monohydroxyalkyl radical, a C₂-C₄ polyhydroxyalkyl radical, a (C₁-C₄)alkoxy(C₁-C₄)alkyl radical and a C₁-C₄ alkyl radical substituted with a nitrogenous group;
- R₁₂ is chosen from a hydrogen atom, a halogen atom, a C₁-C₄ alkyl radical, a C₁-C₄ monohydroxyalkyl radical, a C₁-C₄ hydroxyalkoxy radical, an acetylamino(C₁-C₄)alkoxy radical, a mesylamino(C₁-C₄)alkoxy radical and a carbamoylamino(C₁-C₄)alkoxy radical,
- R₁₃ is chosen from a hydrogen atom, a halogen atom and a C₁-C₄ alkyl radical.
- 35. A composition according to Claim 34, wherein said halogen atom is chosen from chlorine, bromine, iodine and fluorine.
- 36. A composition according to Claim 33, wherein said para-phenylenediamine of formula (III) is chosen from para-phenylenediamine, para-tolylenediamine, 2-chloro-para-phenylenediamine, 2,3-dimethyl-para-phenylenediamine, 2,6-dimethyl-para-phenylenediamine, 2,6-dimethyl-para-phenylenediamine, 2,5-dimethyl-para-phenylenediamine, N,N-diethyl-para-phenylenediamine, N,N-diethyl-para-phenylenediamine, N,N-diethyl-3-methylaniline, N,N-bis(β-hydroxyethyl)-para-phenylenediamine, 4-N,N-bis(b-hydroxyethyl)amino-2-methylaniline, 4-N,N-bis(b-hydroxyethyl)amino-2-chloroaniline, 2-b-hydroxyethyl-para-phenylenediamine, 2-isopropyl-para-phenylenediamine, N-(b-hydroxypropyl)-para-phenylenediamine, 2-hydroxymethyl-para-phenylenediamine, N-(b-hydroxypropyl)-para-phenylenediamine, N-ethyl-N-(b-

Pulson Book hydroxyethyl)-para-phenylenediamine, N-(b,g-dihydroxypropyl)-para-phenylenediamine, N-(4'-aminophenyl)-para-phenylenediamine, N-phenyl-para-phenylenediamine,

2-b-hydroxyethyloxy-para-phenylenediamine, 2-b-acetylaminoethyloxy-para-phenylenediamine, N-(b-methoxyethyl)-para-phenylenediamine, and addition salts thereof

with an acid.

37. A composition according to Claim 33, wherein said double base is chosen from a compound of formula (IV), and an addition salt thereof with an acid:

in which:

Z₁ and Z₂, which are identical or different, are chosen from a hydroxyl radical and an
 -NH₂ radical, each of which is unsubstituted or substituted with a C₁-C₄ alkyl radical or with a linker arm Y;

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- R_{14} and R_{15} are chosen from a hydrogen atom, a halogen atom, a C_1 - C_4 alkyl radical, a C_1 - C_4 monohydroxyalkyl radical, a C_2 - C_4 polyhydroxyalkyl radical, a C_1 - C_4 aminoalkyl radical and a linker arm Y;
- R₁₆, R₁₇, R₁₈, R₁₉, R₂₀ and R₂₁, which are identical or different, are chosen from a hydrogen atom, a linker arm Y and a C₁-C₄ alkyl radical;
- said linker arm Y is chosen from a linear alkylene chain and a branched alkylene chain, each chain comprising from 1 to 14 carbon atoms, which can be interrupted or terminated with at least one nitrogenous group, at least one hetero atom, or a mixture thereof and optionally substituted with at least one hydroxyl radical or a C₁-C₆ alkoxy radical;

with the proviso that said compounds of formula (IV) comprise only one linker arm Y per molecule.

- 38. A composition according to Claim 37, wherein said at least one hetero atom is chosen from oxygen, sulphur and nitrogen.
- 39. A composition according to Claim 37, wherein said double base of formula (IV) is chosen from N,N'-bis(b-hydroxyethyl)-N,N'-bis(4'-aminophenyl)-1,3-diaminopropanol, N,N'-bis(b-hydroxyethyl)-N,N'-bis(4'-aminophenyl)ethylenediamine, N,N'-bis(4-aminophenyl) ethylenediamine, N,N'-bis(4-aminophenyl) ethylenediamine, N,N'-bis(4-aminophenyl) ethylenediamine, N,N'-bis(4-aminophenyl) bis(ethyl)-N,N'-bis(4'-amino-3'-methylphenyl)ethylenediamine, 1,8-bis(2,5-diaminophenoxy)-3,5-dioxaoctane, and an addition salt thereof with an acid.

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40. A composition according to Claim 33, wherein said para-aminophenol is chosen from a compound of formula (V), and an addition salt thereof with an acid:

$$\begin{array}{c|c} \text{OH} & \\ \hline & R_{22} \\ \hline & R_{23} \\ \text{NH}_2 \end{array} \hspace{0.5cm} \text{(V)}$$

in which:

- R₂₂ is chosen from a hydrogen atom, a halogen atom, a C₁-C₄ alkyl radical, a C₁-C₄ monohydroxyalkyl radical, a (C₁-C₄)alkoxy(C₁-C₄)alkyl radical, a C₁-C₄ aminoalkyl radical and a hydroxy(C₁-C₄)alkylamino(C₁-C₄)alkyl radical,
- R₂₃ is chosen from a hydrogen atom, a halogen atom, a C₁-C₄ alkyl radical, a C₁-C₄ monohydroxyalkyl radical, a C₂-C₄ polyhydroxyalkyl radical, a C₁-C₄ aminoalkyl radical, a cyano(C₁-C₄)alkyl radical and a (C₁-C₄)alkoxy(C₁-C₄)alkyl radical, with the proviso that at least one of the substituents R₂₂ and R₂₃ is a hydrogen atom.
- 41. A composition according to Claim 40, wherein said para-aminophenol of formula (V) is chosen from para-aminophenol, 4-amino-3-methylphenol, 4-amino-3-hydroxymethylphenol, 4-amino-2-methylphenol, 4-amino-2-methylphenol, 4-amino-2-aminomethylphenol, 4-amino-2-aminomethylphenol

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amino-2-(b-hydroxyethylaminomethyl)phenol, 4-amino-2-fluorophenol, and an addition salt thereof with an acid.

- 42. A composition according to Claim 33, wherein said ortho-aminophenol is chosen from 2-aminophenol, 2-amino-5-methylphenol, 2-amino-6-methylphenol, 5-acetamido-2-aminophenol, and an addition salt thereof with an acid.
- 43. A composition according to Claim 33, wherein said heterocyclic oxidation bases are chosen from a pyridine derivative, a pyrimidine derivative, a pyrazole derivative, and an addition salt thereof with an acid.
- 44. A composition according to Claim 26, wherein said at least one oxidation base is present in an amount ranging from about 0.0005 to about 12% by weight relative to the total weight of the dye composition.
- 45. A composition according to Claim 44, wherein said at least one oxidation base is present in an amount ranging from about 0.005 to about 6% by weight relative to the total weight of the dye composition.
- 46. A composition according to Claim 26, wherein said at least one 3-aminopyridine derivative of formula (I) is chosen from:
- 4'-dimethylaminobenzene-1'-azo-1-methyl-3-pyridinium methosulphate of formula:

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- 4'-bis(b-hydroxyethyl)aminobenzene-1'-azo-1-methyl-3-pyridinium methosulphate of formula:

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 4'-dimethylamino-2'-nitrobenzene-1'-azo-1-methyl-3-pyridinium methosulphate of formula:

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- 4'-aminobenzene-1'-azo-3-pyridine N-oxide of formula:

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- 4'-dimethylaminobenzene-1'-azo-3-pyridine N-oxide of formula:

- 4'-N,N-bis(b-hydroxyethyl)aminobenzene-1'-azo-3-pyridine N-oxide of formula:

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$$CH_3$$
 N
 CH_3
 $C_2H_5SO_4$
 CH_3

- 4'-dimethylamino-2'-methylbenzene-1'-azo-1-butyl-3-pyridinium bromide of formula:

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- 2',4'-diamino-5'-methylbenzene-1'-azo-1-methyl-3-pyridinium methosulphate of formula:

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$$CH_3$$
 NH_2
 NH_2
 CH_3SO_4

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 4'-phenylaminobenzene-1'-azo-1-methyl-3-pyridinium methosulphate of formula:

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- 2'-acetylamino-4'-dimethylaminobenzene-1'-azo-1-ethyl-3-pyridinium ethosulphate of formula:

- 2',4'-diamino-5'-methoxybenzene-1'-azo-1-methyl-3-pyridinium methosulphate of formula:

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- 2'-amino-4'-dimethylaminobenzene-1'-azo-1-methyl-3-pyridinium methosulphate of formula:

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- 47. A composition according to Claim 26, wherein said at least one 3-amino-pyridine derivative of formula (I) is present in an amount ranging from about 0.001 to about 10% by weight relative to the total weight of the dye composition.
- 48. A composition according to Claim 47, wherein said at least one 3-aminopyridine derivative of formula (I) is present in an amount ranging from about 0.01 to about 5% by weight relative to the total weight of the dye composition.
- 49. A composition according to Claim 26, wherein said meta-aminophenol derivative of formula (II) is chosen from 5-amino-2-methoxyphenol, 5-amino-2-(b-hydroxyethyloxy)phenol, 5-amino-2-methylphenol, 5-N-(b-hydroxyethyl)amino-4-methoxy-2-methylphenol, 5-amino-4-methoxy-2-methylphenol, 5-amino-4-methoxy-2-methylphenol, 5-amino-4-chloro-2-methylphenol, 5-amino-2,4-dimethoxyphenol, 5-(g-hydroxypropylamino)-2-methylphenol, 3-amino-2-chloro-6-methylphenol, 3-amino-6-chlorophenol, 3-(b-aminoethyl)amino-6-chlorophenol, and an addition salt thereof with an acid.
- 50. A composition according to Claim 26, wherein said meta-aminophenol derivative of formula (II) is present in an amount ranging from about 0.0001 to about 10% by weight relative to the total weight of the dye composition.
- derivative of formula (II) is present in an amount ranging from about 0.005 to about 5% by weight relative to the total weight of the dye composition.

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- 52. A composition according to Claim 26, further comprising at least one coupler other than said meta-aminophenol derivative of formula (II), at least one direct dye other than said 3-aminopyridine derivatives of formula (I), or a mixture thereof.
- 53. A composition according to Claim 26, wherein said addition salt with an acid is chosen from a hydrochloride, a hydrobromide, a sulphate, a tartrate, a lactate and an acetate.
- 54. A composition according to Claim 26, wherein said composition is in a medium suitable for dyeing.
- 55. A composition according to Claim 54, wherein said medium suitable for dyeing comprises water or a mixture of water and at least one organic solvent.
- 56. A composition according to Claim 26, wherein said composition has a pH ranging from about 3 to about 12.
 - 57. A process for dyeing keratin fibers comprising:
- 1) applying at least one dye composition to keratin fibers, wherein said at least one dye composition comprises
 - a) at least one oxidation base,
 - b) as a direct dye, at least one 3-aminopyridine derivative chosen from the compounds of formula (I):

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in which:

- B is chosen from formula (la) and (lb):

$$N$$
(Ia)
 N
 X
(Ib)

- R is a C₁-C₄ alkyl radical;
- R₁ is chosen from a hydrogen atom, a halogen atom, a C₁-C₄ alkyl radical, and a C₁-C₄ alkoxy radical;
- R_2 is chosen from a hydrogen atom, a C_1 - C_4 alkyl radical, and a C_1 - C_4 alkoxy radical;

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- R₄ is chosen from a hydrogen atom, a halogen atom, a C₁-C₄ alkyl radical, a nitro, an amino radical and a (C₁-C₄)acylamino radical;
- R₃ is a hydrogen atom, or R₄ and R₃ together form a 6-membered unsaturated ring bearing a hydroxyl substituent chelated with one of the nitrogen atoms of the azo double bond;
- A is a residue -NR₅R₆ in which R₅ is chosen from a hydrogen atom, a C₁-C₄ alkyl radical, a C₁-C₄ monohydroxyalkyl radical and a C₂-C₄ polyhydroxyalkyl radical and R₆ is chosen from a hydrogen atom, a C₁-C₄ alkyl radical, a C₁-C₄ monohydroxyalkyl radical, a C₂-C₄ polyhydroxyalkyl radical, a phenyl ring and a -CH₂-SO₃Na radical;
- X is chosen from a monovalent anion and a divalent anion, and
 c) at least one coupler chosen from a meta-aminophenol derivative of formula (II), and
 an addition salt thereof with an acid:

$$\begin{array}{c} \text{OH} \\ \text{R}_9 \\ \text{NHR}_7 \end{array} \qquad \text{(II)}$$

in which:

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- R₇ is chosen from a hydrogen atom, a C₁-C₄ alkyl radical, a C₁-C₄ monohydroxyalkyl radical, a C₂-C₄ polyhydroxyalkyl radical and a C₁-C₄ monoaminoalkyl radical;
- R₈ is chosen from a hydrogen atom, a halogen atom, a C₁-C₄ alkyl radical and a C₁-C₄ alkoxy radical;
- R₉ and R'₉, which are identical or different, are chosen from a hydrogen atom, a halogen atom, a C₁-C₄ alkyl radical, a C₁-C₄ alkoxy radical, a C₁-C₄ monohydroxyalkyl radical, a C₂-C₄ polyhydroxyalkyl radical, a C₁-C₄ monohydroxyalkoxy radical and a C₂-C₄ polyhydroxyalkoxy radical;

with the proviso that at least one of the substituents R_7 , R_8 , R_9 and R'_9 is not a hydrogen atom; and

- 2) developing a color at an acidic, neutral or alkaline pH with the aid of an oxidizing agent, wherein said oxidizing agent is added to said at least one dye composition at the time of application of said at least one dye composition, or wherein said oxidizing agent is present in an oxidizing composition, and wherein said oxidizing composition is applied simultaneously or sequentially with said at least one dye composition.
- 58. A process according to Claim 57, wherein said oxidizing agent present in the oxidizing composition is chosen from hydrogen peroxide, urea peroxide, alkali metal bromates, persalts, peracids and enzymes.
- 59. A process according to Claim 58, wherein said persalts are chosen from perborates, percarbonates and persulphates.

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- 60. A multi-compartment dyeing device or kit comprising at least two compartments, wherein one compartment comprises an oxidizing composition, and another compartment comprises at least one dye composition, wherein said at least one dye composition comprises
 - a) at least one oxidation base,
 - b) as direct dye, at least one 3-aminopyridine derivative chosen from the compounds of formula (I):

$$\begin{array}{c|c}
R_2 \\
N = N \\
R_4 \\
R_3
\end{array}$$
(I)

in which:

- B is chosen from formula (la) and (lb):

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- R is a C₁-C₄ alkyl radical;
- R₁ is chosen from a hydrogen atom, a halogen atom, a C₁-C₄ alkyl radical, and a
 C₁-C₄ alkoxy radical;
- R₂ is chosen from a hydrogen atom, a C₁-C₄ alkyl radical, and a C₁-C₄ alkoxy radical;
- R₄ is chosen from a hydrogen atom, a halogen atom, a C₁-C₄ alkyl radical, a nitro, an amino radical and a (C₁-C₄)acylamino radical;
- R₃ is a hydrogen atom, or R₄ and R₃ together form a 6-membered unsaturated ring bearing a hydroxyl substituent chelated with one of the nitrogen atoms of the azo double bond;
- A is a residue -NR $_5$ R $_6$ in which R $_5$ is chosen from a hydrogen atom, a C $_1$ -C $_4$ alkyl radical, a C $_1$ -C $_4$ monohydroxyalkyl radical and C $_2$ -C $_4$ polyhydroxyalkyl radical and R $_6$ is chosen from a hydrogen atom, a C $_1$ -C $_4$ alkyl radical, a C $_1$ -C $_4$ monohydroxyalkyl radical, a C $_2$ -C $_4$ polyhydroxyalkyl radical, a phenyl ring and a -CH $_2$ -SO $_3$ Na radical;
- X is chosen from a monovalent anion and a divalent anion, and
 c) at least one coupler chosen from a meta-aminophenol derivative of formula (II),
 and an addition salt thereof with an acid:

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